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LAMINATED WOOD-BASED COMPOSITES
TO
MASS TRANSFER

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Petroleum Lubricants

Lubricating oils from petroleum consist essentially of complex mixtures of hydrocarbon molecules (see Petroleum). These generally range from low viscosity oils with molecular weights as low as 250 to very viscous lubricants with molecular weights as high as about 1000. Physical properties, such as viscosity, viscosity–temperature–pressure characteristics, and performance, depend largely on the relative distribution of paraffinic, aromatic, and alicyclic (naphthenic) components. Typical structures of the hydrocarbons that are present in lubricating oils are indicated in Figure 6 (13). For a given molecular size, the paraffins have relatively low viscosity and density and higher freezing points as compared to the other types. Paraffinic oils have low oxidation resistance unless properly inhibited, in which case they offer high stability with little tendency for sludging. Although aromatics have a high degree of oxidation stability, they form insoluble black sludges at high temperatures. Aromatic oils also are characterized by a relatively rapid change in viscosity with temperature, high density, and darker color. Alicyclic oils are characterized by a low pour point, low order of oxidation stability, and other physical properties that are intermediate to those of the paraffins and aromatics. Almost all of the so-called paraffinic oils are composed of both paraffinic and alicyclic structures, with only a minor proportion of aromatics. When stabilized with an oxidation inhibitor, alicyclics offer nonsludging oils that are satisfactory for almost any type of service. Excellent means are available for determining the proportion of structural types that are present; these include adsorption and other separational techniques in combination with measurement of density, refractive index, molecular weight, and spectroscopic characteristics. Detailed analysis is obtained by mass spectroscopy (13).

In distillation of petroleum crude oils, the lower boiling gasoline, kerosene, and fuel oils are removed first, and the lubricating-oil fractions are divided by boiling-point

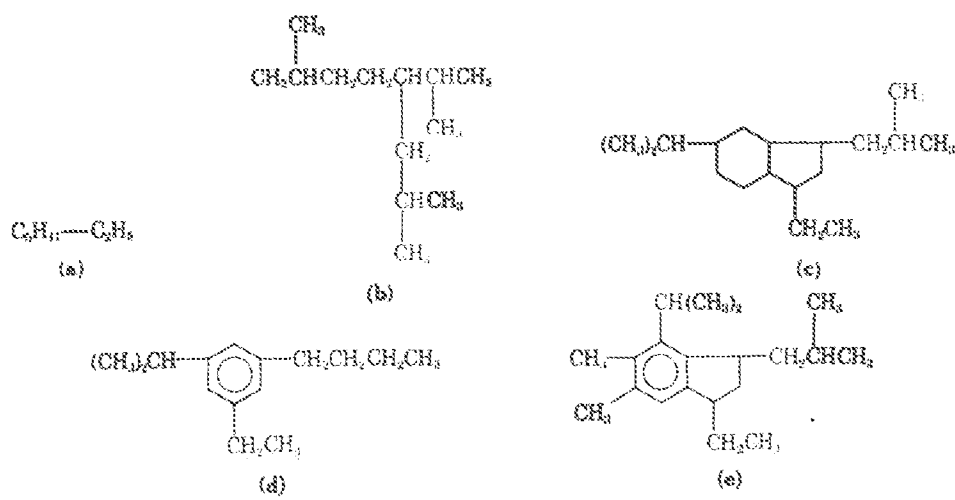

Figure 6. Typical structures in lube oil: (a) *n*-paraffin, (b) isoparaffin, (c) cycloparaffin, (d) aromatic hydrocarbon, (e) mixed aliphatic and aromatic ring (13).

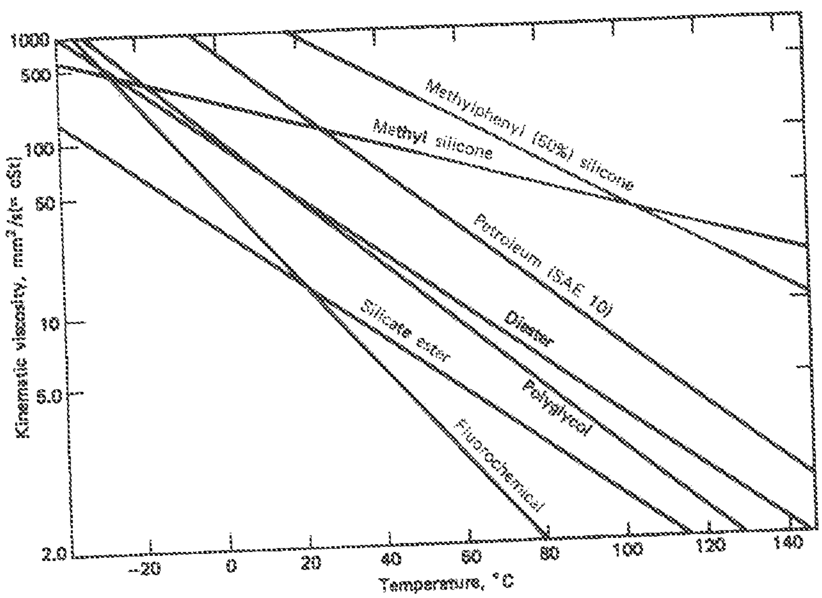

Figure 13. Viscosity–temperature characteristics of various fluids.

In addition to their good high temperature stability, the silicate esters have good viscosity–temperature characteristics and low pour points and generally are intermediate in characteristics between the diester oils and the silicones. Their poor hydrolytic stability has interferred with their general application.

Fluorochemicals. Fluorochemicals, such as poly(chlorotrifluoroethylene), copolymers of perfluoroethylene and perfluoropropylene, have been used to achieve maximum resistance to oxidation (38). These fluids generally have poor low-temperature properties and poor viscosity–temperature characteristics. With their relatively poor lubricating properties and high price, they have limited use except where their inertness is necessary under extreme oxidation conditions, eg, in equipment for manufacturing and handling liquid oxygen and hydrogen peroxide (see Fluorine compounds, organic).

Greases

A grease is a lubricating oil that is thickened with a gelling agent, eg, a soap (qv). Because of design simplicity, decreased sealing requirements, and less need for maintenance (40), greases almost universally are given first consideration for ball and roller bearings in electric motors, household appliances, automotive wheel bearings, machine tools, aircraft accessories, and railroad apparatus. They also are used for the lubrication for small gear drives and for many slow-speed sliding applications.

Oils in Greases. Essentially the same type of oil is employed in compounding a grease as would normally be selected for oil lubrication. Petroleum oils are used in over 99% of the greases produced and commonly range from SAE 20–30. Less viscous oils, with viscosities down to 25 mm²/s (= cSt) at 40°C and lower, are used in some special

greases at low temperatures, and some quite viscous oils in the range of 450–650 mm^2/s are employed for high temperatures. Oils of about 100–130 mm^2/s viscosity at 40°C are the usual choice. Such an oil provides satisfactory low volatility for long life at elevated temperatures (41) and provides low torque down to subzero temperatures. The maximum oil viscosity in a grease for starting medium-torque equipment is about 100,000 mm^2/s (4). Extrapolations for various oils can be made on viscosity–temperature charts, as shown in Figure 8, to estimate the approximate low temperature limit with various petroleum oils that are used in greases.

Although oils derived from many crudes and refined by widely different processes are used in making greases, less highly refined oils and the alicyclic types are the most widely used and are more adaptable to grease compounding (42).

Thickeners. Common gelling agents are the fatty-acid soaps of lithium, calcium, sodium, aluminum, and barium in concentrations of 8–25 wt % (42); the growth in the use of lithium greases has been the greatest. From initial commercial production in 1942, their use has expanded to comprise about 55% of the total market (43). The fatty acids that are employed in forming the soaps usually are oleic, palmitic, stearic, and other carboxylic acids derived from tallow, hydrogenated fish oil, castor oil and, less often, wool grease and rosin. The relatively low upper temperature limit with conventional calcium and aluminum greases has been significantly raised through new complex soap formulations. Calcium-complex greases commonly include a minor proportion of calcium acetate [*62-54-4*] with the fatty acid soap thereby forming multipurpose greases with dropping points above 260°C. An aluminum-complex grease can be made from the reaction of a combination of stearic and benzoic acids and a reactive aluminum compound such as aluminum isoperoxide (42).

Finely divided clay particles of the bentonite and hectorite types commonly are used after being given a surface coating with organic materials such as quaternary ammonium compounds (qv) (see Clays, uses). Many of these clay-thickened greases are manufactured readily by simple mixing. Such greases have been produced with high melting points, excellent water resistance, and long life for multipurpose application in industrial and automotive equipment. Carbon black is used as a thickener in some high temperature petroleum and synthetic greases. Organic powders and pigments, which are stable at elevated temperatures, are being used increasingly. Arylurea compounds are used in petroleum greases for ball bearings at temperatures up to about 150°C (43). Indanthrene [*81-77-6*], phthalocyanines, and ureides also have been used.

Although the gelling action of all thickening agents is not completely understood, most of the soap type are fibrous crystallites. Oil is believed to be held in the fibrous structure by a combination of capillary forces, adsorption on the gel-forming molecules, and physical entrapment within the interlacing fiber structure. The relative importance of each of these mechanisms depends on the type and degree of dispersion of the thickener, the type and solvency action of the oil, and the influence of any stabilizing agents and additives. The wide variation and characteristics that can be obtained in petroleum greases with various thickener types is indicated in Table 10.

Additives. Chemical additives similar to those used in lubricating oils also are added to grease to improve oxidation resistance, rust protection, and extreme pressure properties (44). Although 1-naphthyl(phenyl)amine is the common choice as an oxidation inhibitor at about 0.1–0.5% concentration, other amine, phenolic, phosphite, sulfur, and selenium inhibitors also are used. A common procedure involves trying